

Haloacetic Acids (HAAs) in the Central Waterworks in Warsaw, Poland

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Abstract

The results of the study of HAAs formation in the Central Waterworks in Warsaw, Poland are presented. Water was taken from the Vistula River by two methods: infiltration and bank intake, then treated in two parallel water treatment systems using different technologies. Water was analyzed during various steps of treatment and the following parameters were determined: HAAs, COD-Mn, colour, TOC, UV_{254} absorbance and temperature. The removal of organic substances during water treatment was presented. Water was disinfected with chlorine, chlorine dioxide or a mixture of the two. It was found that formation of haloacetic acids depended on water temperature, organic precursors of HAAs and disinfectant type. The study was performed from January 2002 to January 2003. The highest concentration of HAAs was noticed in May and September.

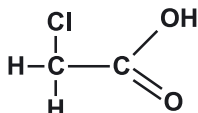
Keywords: haloacetic acids (HAAs), disinfection by-products (DBPs), natural organic matter, water disinfection

Introduction

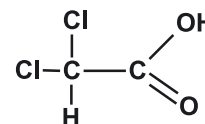
Haloacetic acids (HAAs) are formed during water chlorination. Natural organic matter (NOM) occurring in water (mainly humic acids as well as other natural and anthropogenic organic substances) are transformed by chlorine compounds that form haloacetic acids, mostly chloroacetic acids like monochloroacetic acid (MCAA), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA).

Main haloacetic acids formed during water disinfection are as follows:

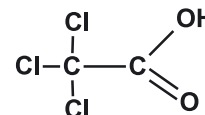
monochloroacetic acid (MCAA)



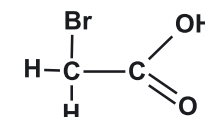
dichloroacetic acid (DCAA)



trichloroacetic acid (TCAA)

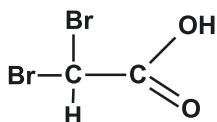


monobromoacetic acid (MBAA)



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dibromoacetic acid (DBAA)



Haloacetic acids are found in much of the world's drinking waters, mainly in waterworks that take surface water. Detected sum of HAAs in drinking water ranges from low concentrations – 0.14 µg/L [1] to high ones reaching 140 µg/L [2]. Uden et al. [3] found TCAA and DCAA in U.S. tap water in concentrations up to 160 µg/L. Norwood et al. [4] reported TCAA concentrations in the range of 4-54 µg/L for drinking water in North Carolina (USA). Peters et al. [5] found the sum of HAAs in the range of 3.8-14.7 µg/L in Dutch drinking water prepared from surface water. Villanueva et al. [6] found the sum of HAAs in the range of 3-50 µg/L in drinking water samples taken from four Spanish regions.

The problems of HAAs, which are the most common of DBPs (disinfection by-products) usually concern waterworks using surface water. Studies are carried out on how to diminish concentration of DBPs in drinking water for consumers. The studies focused on removal of organic compounds which are precursors of HAAs and on new disinfection technology.

Haloacetic acids are harmful to people. For example, the study carried out on experimental animals showed that dichloroacetic and trichloroacetic acids are potential animal carcinogens. This is in agreement with results obtained by Clack [7] and Kim [8].

The permissible concentration of HAAs in drinking water is as follows:

- Standard of US EPA [9]
 - sum of five HAAs – 60 µg/L,
- Directives of WHO [10]
 - dichloroacetic acid – 50 µg/L,
 - trichloroacetic acid – 100 µg/L,
- Disposition of the Polish Ministry of Health [11]
 - monochloroacetic acid – 30 µg/L.

Aim of the Study

Disinfection of water in Central Waterworks in Warsaw is performed with the use of gaseous chlorine and chlorine dioxide. As a result of disinfection process, the disinfection by-products are formed. Sometimes haloacetic acids (HAAs) are in the concentration exceeding permissible values. The aim of this study was to learn the reason for HAAs formation, especially to find the relationships between quality of raw water, technological processes of water treatment, quality of water before disinfection and methods and procedures of water disinfection.

Description of the Central Waterworks in Warsaw

Water is taken from the Vistula River in two ways: infiltration and bank intake (Fig.1). Infiltration consists on water filtration through natural river bed 6-7 m thick. After bank intake, water flows to sedimentation pond with surface about 18 ha. In the Central Waterworks water is treated on two parallel water treatment systems, with different technological processes.

Water Treatment System I

This system works only with infiltration water. The treatment is based on rapid filtration on the sand and gravel beds and then on slow filtration. Slow filters have 10 cm layers of activated carbon. In this system about 70% of water is produced, which is treated in the Central Waterworks.

Water Treatment System II

Raw surface water from the Vistula River (about 60%) and infiltration water (about 40%) is supplied to this system. Water treatment is based on coagulation and rapid filtration on sand filters. Coagulation is carried out in pulsators with such reagents as aluminium sulphate and activated silica. About 30% of water which is treated in the waterworks is produced in this system

Disinfection

Water was chlorinated separately in both water treatment systems. Water disinfection was made with a mixture of chlorine (Cl₂) and chlorine dioxide (ClO₂) with a tendency to use more ClO₂. There was a limitation that drinking water could contain no more than 0.4 mg/L of chlorite.

Materials and Methods

The concentrations of HAAs precursors were determined by a measure of water quality parameters like colour, TOC (total organic carbon), COD-Mn (chemical oxygen demand by permanganate method) and UV₂₅₄ absorbance (ultraviolet spectrophotometry – indicator of dissolved organic matter). Those water quality parameters were measured immediately after sampling by the commonly used method described in the Polish Standards. Simultaneously, water temperature was measured.

Water samples were taken from the following points (see scheme of water treatment, Fig.1):

1. Water in the Vistula River (raw water),
2. Water after sedimentation pond,
3. Water after filtration,
4. Water after treatment in the water treatment system I,
5. Water after treatment in the water treatment system II,
6. Water after disinfection (finished water).

The study was performed once a month from January 2002 to January 2003. The haloacetic acids MCAA, MBAA, DCAA, TCAA and DBAA were determined in water after disinfection. The procedure of HAAs determination was based on the method described in the Standards Methods [12]. The haloacetic acids were extracted from water samples with methyl tertiary-butyl ether (MTBE). To increase extraction efficiency, a salting agent was added. The extracted compounds were esterified with a diazomethane solution to produce methyl ester derivatives. The obtained methyl derivatives were determined using gas chromatography with a capillary column and electron capture detector (ECD). Detection limits for haloacetic acids are as follows: MCAA – 0.082 µg/L, MBAA – 0.087 µg/L, DCAA – 0.054 µg/L, TCAA – 0.054 µg/L and DBAA – 0.065 µg/L [12].

Discussion of Results

Changes of HAAs Precursors (Colour, TOC, COD-Mn and UV₂₅₄ Absorbance) During Water Treatment

Decrease of concentration of HAAs precursors during infiltration process was 2-3 times higher than removal in the sedimentation pond (table 1). Water after filtration and after sedimentation pond was treated on two parallel water treatment systems. Water temperature during treatment

processes changed slightly, and drinking water temperature pumped to the municipal network was no higher 1°C from the temperature of raw water. During the treatment, removal of organics characterized by the parameters of colour, TOC, COD – Mn and UV₂₅₄ absorbance was observed (Table 2).

Water pumped to water treatment system I had better quality (it was only filtration water) than water pumped to system II (mixed: after sedimentation pond – 60%, and after filtration – 40%). But treatment processes in system II were removing organic pollutants at a higher stage than waters leaving both systems.

Influence of Water Quality and Ways of Disinfection on HAAs Concentrations

Water temperature varied throughout the year from 0.5°C to 25°C.

The concentrations of HAAs changed too, depending on the season of the year. The highest concentrations were found in the periods when water temperature was high (Fig.2). But it is connected not only with temperature, but also with the seasons of the year. In seasons when water was warm, the content of organic matter was the highest, which can influence the formation of HAAs.

The influence of temperature on formation of HAAs was studied in the USA [13]. The concentration of the sum

Table 1. Changes of water quality after infiltration and sedimentation pond (yearly average).

Parameters	Sampling point	Water after filtration, (point 3)			Water after sedimentation pond, (point 2)	
	Vistula water, (point 1)	concentration, mg/L	removal, %	concentration, mg/L	removal, %	
Colour, mg/L Pt	23	14	39	20	13	
COD – Mn, mg/L O ₂	7.9	3.8	52	5.7	28	
UV ₂₅₄ absorbance, m ⁻¹	15.4	10.7	31	13.6	12	

Table 2. Removal of organic substances during water treatment (yearly average).

Parameters	Sampling point	I water treatment system			II water treatment system		
	before treatment, (point 3)	after treatment, (point 4)	removal, %	before treatment, (point 2)	after treatment, (point 5)	removal, %	
Colour, mg/L Pt	14	6	57	20	6	70	
TOC, mg/L C	3.9	3.2	18	5.1	3.1	39	
COD – Mn, mg/L O ₂	3.8	2.95	22	5.7	2.8	51	
UV ₂₅₄ absorbance, m ⁻¹	10.7	7.1	34	13.6	6.2	54	

of six HAAs increased from about 50 µg/L (at 10°C) to about 100 µg/L (at 35°C). Mainly, the concentrations of MCAA, DCAA and TCAA grew. In other studies [14, 15] it was observed that the highest concentrations of HAAs were noticed in summer, in periods of high temperature and the lowest in winter, which confirm the influence of temperature on HAAs formation.

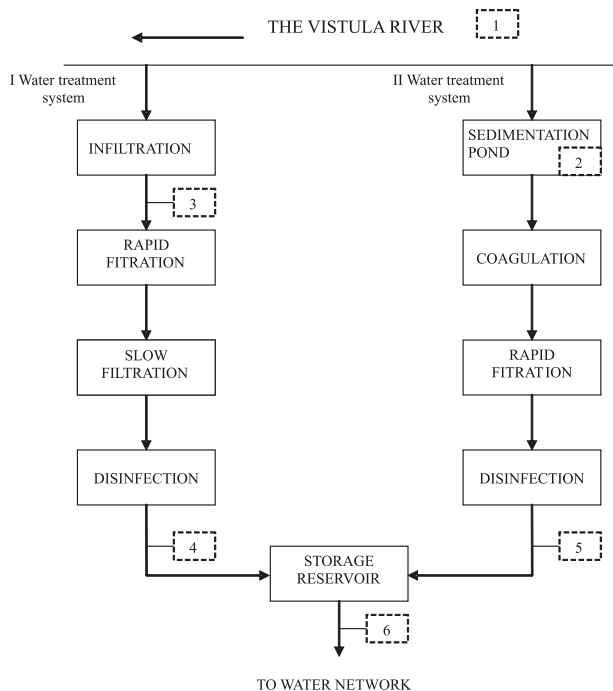


Fig. 1. The scheme of water treatment. Dotted sampling point – 1

Natural organic matter contents in the Vistula River (raw water) expressed by parameters: colour, TOC, COD – Mn and UV₂₅₄ absorbance influenced the formation of HAAs. The relationship was irregular, but generally the highest values of those parameters, the higher concentrations of HAAs were observed. The best relationship was found for UV₂₅₄ absorbance and the sum of HAAs, lower for colour, COD – Mn and sum of HAAs (Fig. 3).

Water was disinfected with chlorine (Cl₂), chlorine dioxide (ClO₂) or a mixture of Cl₂/ClO₂. With the increase of Cl₂ or ClO₂ doses, the concentration of formed HAAs was higher (Fig. 4). The same relationship was observed by Singer et al. [16], during the study of drinking water in six water treatment plants in North Carolina, USA. Most often the mixture of Cl₂ and ClO₂ was used. With the increase of the ClO₂ dose in relationship to Cl₂ one, the concentrations of HAAs were lower. But the use of ClO₂ was limited because concentrations of formed chlorite could not exceed 0.4 mg/L.

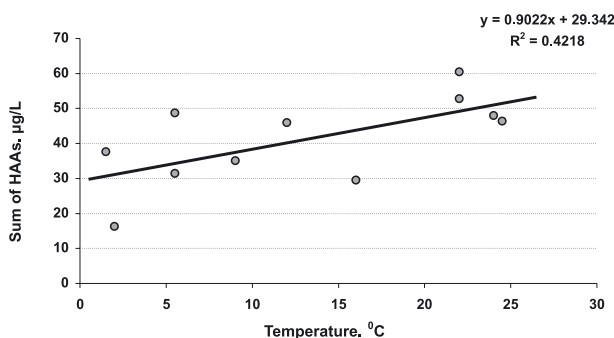


Fig. 2. Relationship between formed HAAs and temperature.

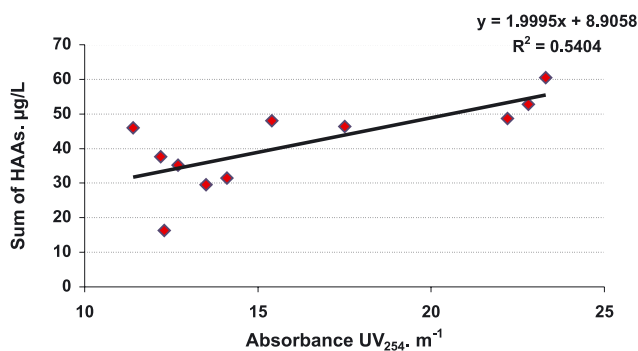
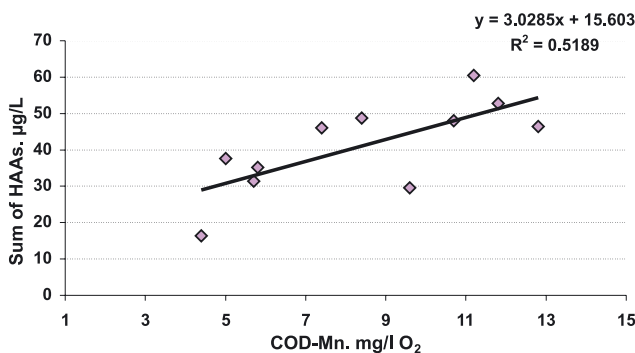
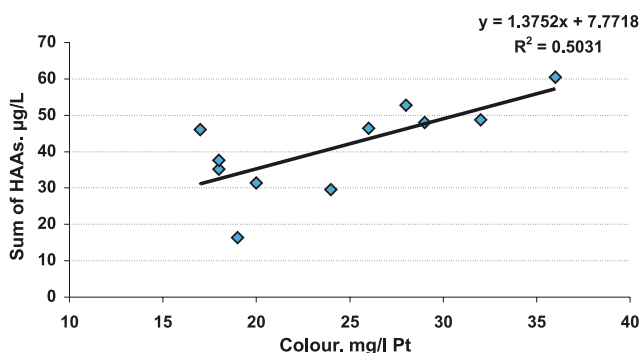


Fig. 3. Relationship between formed HHAs and natural organic matter.

Changes of HAAs Concentrations

The sum of HAAs in water after disinfection was changed from 16.3 µg/L to 60.5 µg/L (Table 3). The highest concentration of HAAs was observed in September 2002 and the lowest in January 2003 (Fig. 5). The changes of concentration of

the individual haloacetic acids varied with time, but in general were the same as for the sum of HAAs. The highest concentration was noticed for MCAA, it was changed from 12.1 µg/L to 40.7 µg/L. The second by turns was DBAA, changing from 2.6 µg/L to 9.6 µg/L. The concentrations of other HAAs were much lower (from 0.4 µg/L to 8.7 µg/L).

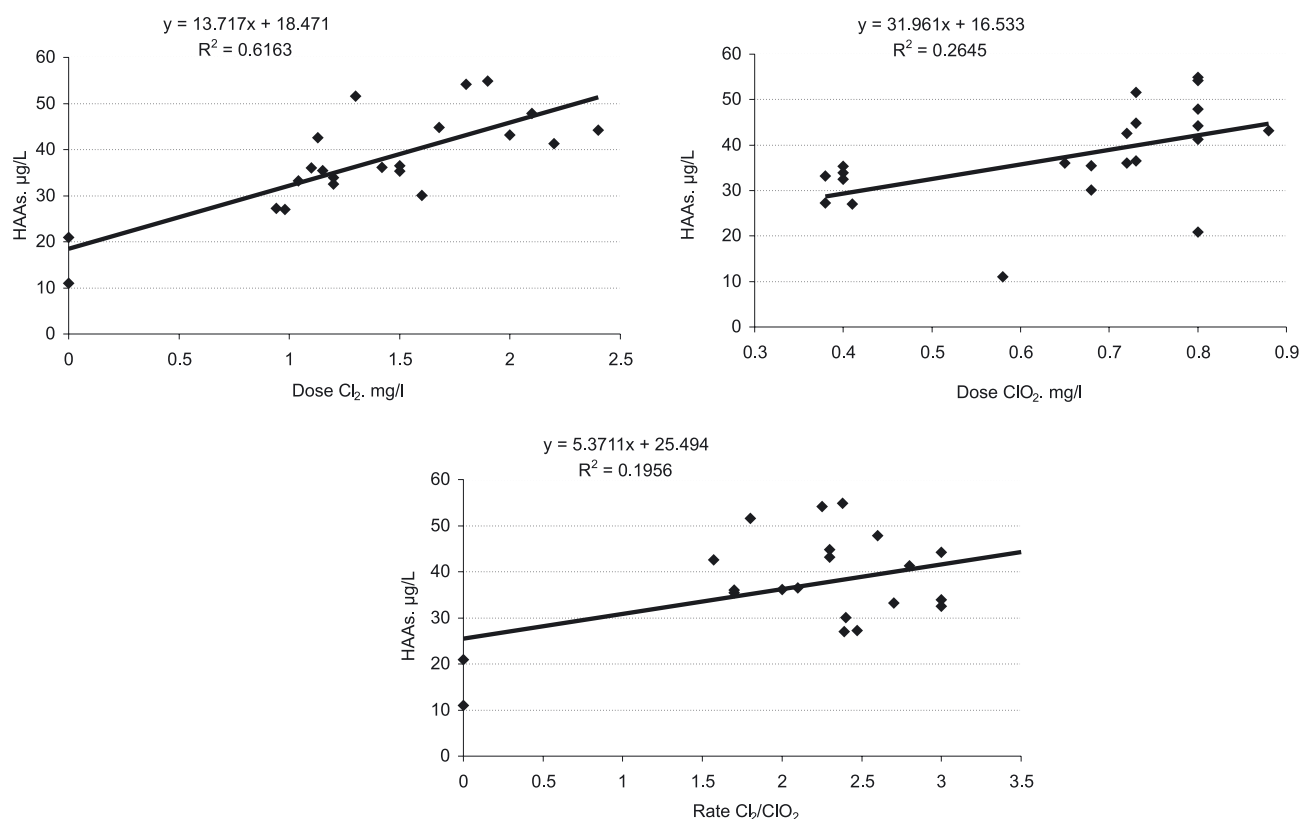


Fig. 4. Relationship between formed HAAs and disinfectant type.

Table 3. HAAs in water after disinfection (finished water), µg/L.

Date	MCAA	DCAA	TCAA	MBAA	DBAA	Σ HAAs
02.2002	27.4	8.7	2.5	5.0	5.1	48.7
04.2002	30.5	1.7	4.1	4.6	5.1	46.0
05.2002	37.2	0.5	4.0	3.7	7.5	52.8
06.2002	17.5	2.5	2.5	2.6	4.5	29.6
07.2002	31.0	1.6	1.7	5.6	6.5	46.4
08.2002	26.0	3.2	3.4	5.9	9.6	48.0
09.2002	40.7	1.5	4.2	5.7	8.5	60.5
10.2002	20.5	1.3	2.1	3.2	8.0	35.1
11.2002	18.8	2.2	1.8	2.2	6.5	31.5
12.2002	22.3	1.4	1.3	6.0	6.6	37.7
01.2003	12.1	0.5	0.7	0.4	2.6	16.3
Average	25.8	2.3	2.6	4.1	6.4	41.2

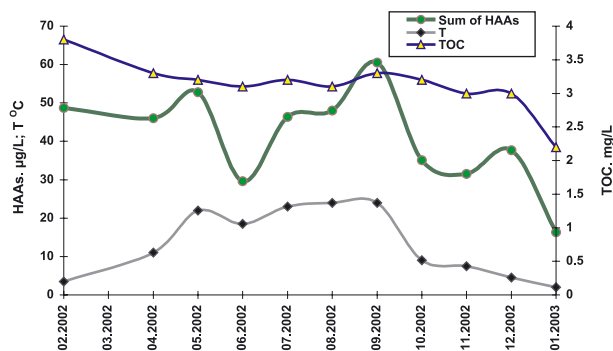


Fig. 5. Sum of HAAs, concentration of TOC and water temperature in finished water.

Conclusions

The haloacetic acids are produced during water chlorination. The sum of formed haloacetic acids in finished water varied from 16.3 µg/L to 60.5 µg/L. The highest concentration was found for MCAA and the second in turns was DBAA. Concentrations of HAAs depended mostly on water temperature and were found in summer.

The formation of haloacetic acids (HAAs) depended on the following water quality parameters and disinfection conditions:

- Water temperature. With the increase of water temperature, concentration of formed HAAs was rising.
- Organic precursors of HAAs. The increase of natural organic matter, expressed by parameters: colour, COD – Mn, TOC and UV_{254} absorbance caused the increase of concentration of formed HAAs.
- Disinfectant type. The smallest amount of HAAs occurred when only ClO_2 was used, and the highest amount by disinfection only with Cl_2 . The mixture of Cl_2/ClO_2 gave the intermediate results, but the increase of Cl_2 caused an increase of formed HAAs.

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